

## BIOMATERIALS

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### POLYMORPHIC TRANSFORMATION OF LEUCITE IN A CRYSTAL-GLASS MATERIAL FOR BIO-CERAMICS

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High-temperature x-ray diffractometry was used to establish the presence of a reversible polymorphic transformation both of synthesized leucite with stoichiometric composition and of leucite precipitated as a result of the crystallization of glass. The temperature limit determined for this transition for leucite in a crystal-glass material shifts to lower temperatures as compared with a modification transition of synthetic leucite.

**Key words:** high-temperature x-ray diffractometry, stoichiometric leucite, crystal-glass material, bioceramic.

A metal-ceramic dental prosthesis consists of a cap made of Ni–Cr or Co–Cr alloys and is coated with three layers of crystal-glass material — opaque, dentine, and enamel.

A basic requirement for the opaque layer of metal-ceramic dental prosthesis is that its CLTE must match that of the metal substrate.

In recent years the most widely used crystal-glass material used for these purposes became leucite glass-ceramic, which the Corning Glass Company (USA) produced commercially under the name Dicor in 1984 [1].

In the present work, a three-component system  $K_2O - Al_2O_3 - SiO_2$ , in which one of the principal crystalline phases is leucite  $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ , shown in [2, 3] to have high mechanical strength and chemical stability, was used to obtain glass-ceramic.

However, aside from these properties, no less important are its CLTE indices, which actively match a coating with a substrate consisting of alloys which likewise have a high CLTE, equal to  $(14.1 - 14.4) \times 10^{-6} K^{-1}$ .

High-temperature diffractometry proved that synthetic leucite can exist in two easily reversible forms [4, 5]. As temperature increases, the crystal lattices expand along the  $a$  axis and compress along the  $c$  axis, which continues to temperature 640°C at which the parameters  $a$  and  $c$  become 13.56 Å, which attests to the completion of the polymorphic transformation associated with a transition of leucite from

the tetragonal into the cubic modification. According to the data of [4–8], the temperatures of this polymorphic transformation lie in the interval 603–625°C.

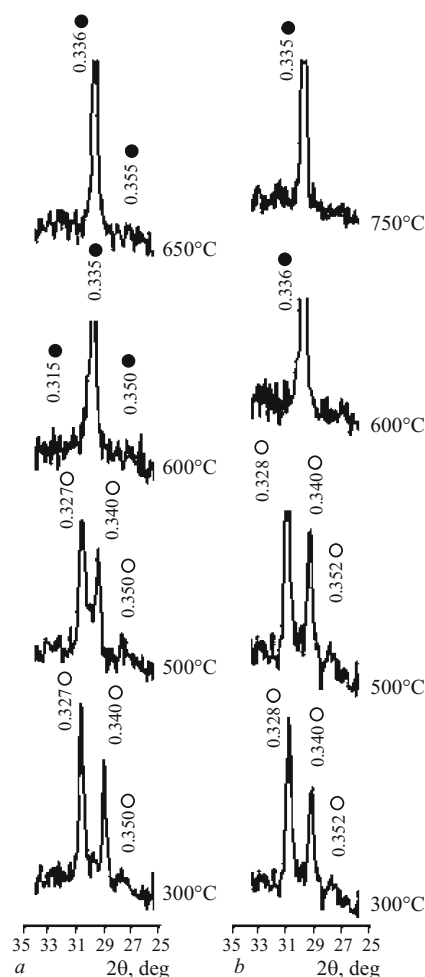
It is important that the CLTEs of the polymorphic forms of leucite — the high-temperature cubic and low-temperature tetragonal — are  $10 \times 10^{-6} K^{-1}$  and  $20 \times 10^{-6} K^{-1}$ , respectively. In addition, according to the data of [9], the computed value of the latter is  $29.5 \times 10^{-6} K^{-1}$ .

The presence of a polymorphic transformation is indicated in recent research performed in [7] studying the thermal expansion and phase transitions in solid solutions of leucite borosilicates of the type  $K_{1-x}Rb_xBSi_2O_6$  and (Cs, Na)-leucite with composition  $Cs_{1-x}Na_xAlSi_2O_6$  ( $x = 0.1, 0.2, 0.3$ ). The difference of the values of the CLTE of the high- and low-temperature forms is even larger in the solid solutions studied:  $(6 - 9) \times 10^{-6} K^{-1}$  and  $(21 - 24) \times 10^{-6} K^{-1}$ , respectively, which gives a basis for supposing that the glass phase affects the polymorphic transformation.

This creates real prerequisites for flexible variation of the CLTE values over a wide range during subsequent heat treatment of the crystal-glass materials as a result of a transition of one polymorphic form of leucite into another as well as changes in the ratio of the residual glassy phase and crystalline leucite. In turn, this can be supposed to affect the properties of the crystal-glass material containing leucite as the principal phase. However, we have not found any published information on the systematic study of this phenomenon.

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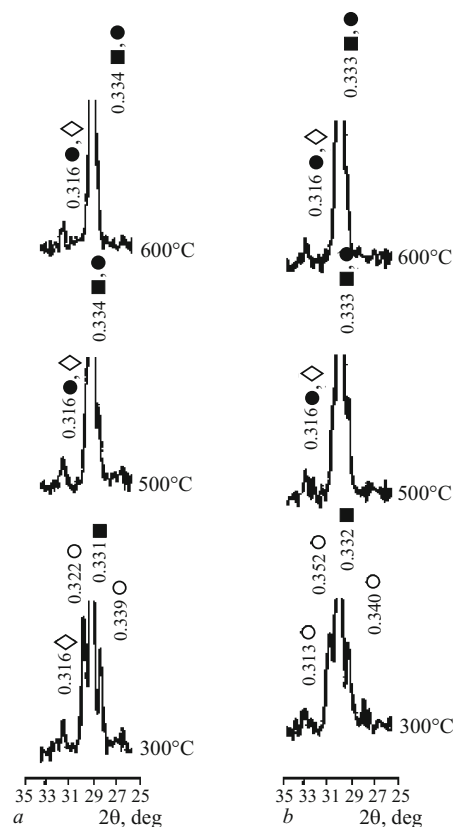
**Fig. 1.** Fragments of high-temperature x-ray diffraction patterns of synthetic leucite on heating (a) and cooling (b): ○) tetragonal leucite; ●) cubic leucite.

The modification transformation was studied on a leucite sample, synthesized according to a definite regime, by means of high-temperature x-ray diffractometry (Fig. 1).

High-temperature diffractometry was performed with a D8 Advance diffractometer (Bruker Company, Germany) with a high-temperature attachment, placed on a goniometer, and  $\text{CuK}\alpha$  radiation.<sup>3</sup>

At higher temperatures, to 600°C, complete coalescence of its main diffraction reflections is observed:  $d = 0.327$  nm (100%) and  $d = 0.340$  nm (70%), attesting to a polymorphic transformation in the interval 500 – 600°C and confirming the data presented in [4 – 8].

Only tetragonal leucite was detected at 500°C in the sample heated at 60 K/min.



**Fig. 2.** Fragments of the high-temperature x-ray diffraction patterns of crystal-glass material on heating (a) and cooling (b): ○) tetragonal leucite; ●) cubic leucite; ■) cassiterite; ◇) baddeleyite.

As the sample cools, this polymorphic transformation starts at 600°C and is detected according to the splitting of the diffraction reflection with  $d = 0.336$  nm (100%). Subsequent cooling results in final conversion of the cubic leucite into the tetragonal modification; this is manifested in the x-ray diffraction pattern, obtained at 500°C, as peaks belonging to the tetragonal modification:  $d = 0.328$  nm (100%) and  $d = 0.340$  nm (70%).

Thus, these results once again confirm that the polymorphic transformation of leucite is reversible.

The second step was concerned with studying the probability of such a transformation occurring in a multiphase crystal-glass material with the composition (wt.%) 51.54  $\text{SiO}_2$ , 11.54  $\text{K}_2\text{O}$ , 11.54  $\text{Al}_2\text{O}_3$ , 2.31  $\text{Li}_2\text{O}$ , 15.4  $\text{SnO}_2$ , 6.15  $\text{ZrO}_2$ , 1.54  $\text{ZnO}$  as the sample is heated at the rate 60 K/min from 20 to 750°C and then cooled at the same rate to 20°C.

It is evident from the x-ray diffraction pattern presented in Fig. 2 that the polymorphic transformation starts at 500°C, which is reflected by the coalescence of the diffraction reflections of leucite  $d = 0.322$  nm (100%) and  $d = 0.339$  nm (70%). The transformation of tetragonal leucite into the cubic modification is recorded at 600°C, which is manifested as the appearance of a peak with interplanar distance  $d = 0.334$  nm (100%).

<sup>3</sup> E. I. Mosunov, senior scientific staff, participated in this study, which was performed at the Laboratory of Nanostructural Materials and Technologies at the State Scientific Institution "Joint Institute of Machine Engineering of the National Academy of Sciences of Belarus."

Interestingly, in this crystal-glass material the polymorphic transformation on heating starts at a lower temperature (500°C) than in synthetic leucite. This suggests that the shift of the temperature intervals of the polymorphic transformation was due to the alloying of the leucite with metal cations, which were present in its crystal lattice, thereby changing its parameters. The formation of solid solutions of leucite as a result of such alloying was also indicated in [4]. It should be assumed that the intermediate layer formed will definitely improve the matching between the matrix glass and a given crystalline phase.

As the crystal-glass material (see Fig. 2) cools from 750 to 20°C, x-ray diffractometry fixes the onset of the transformation of cubic leucite into the tetragonal modification at the temperature 500°C; this is reflected by the splitting of the main reflection of leucite with  $d = 0.333$  nm (100%). The polymorphic transformation is completed at 300–400°C and is reflected in the form of two distinct reflections:  $d = 0.325$  nm (100%) and  $d = 0.340$  (70%). The polymorphic transformation on cooling likewise occurs at lower temperatures as compared with synthetic leucite; this attests to a probable effect of the alloying additives on the structure of the leucite, crystallized in a multicomponent system.

Since the transformation of one modification into another occurs in the temperature interval 500–600°C, this makes possible their simultaneous presence in the samples, as the splitting of the main reflections in the x-ray diffraction patterns indicates. Therefore, the quantitative ratio of both modifications, whose CLTE values differ substantially from one another, can be controlled by varying the heat-treatment temperature.

It should be noted that high-temperature x-ray diffractometry also detects other crystalline phases in the crystal-glass material — cassiterite and baddeleyite, which do not undergo polymorphic transformations on heating and cooling.

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